Control of stoichiometry and observation of spin excitations in the S = 1/2 bilayer triangular lattice antiferromagnet LiZn2Mo3O8

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論　文　内　容　要　旨

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学位論文の題　　目	Control of stoichiometry and observation of spin excitations in the S = 1/2 bilayer triangular lattice antiferromagnet $LiZn_2Mo_3O_8$ (S = 1/2 二層三角格子反強磁性体 $LiZn_2Mo_3O_8$ の化学量論比の制御とスピン励起の観測)		

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INTRODUCTION

Geometrically frustrated quantum magnetism is an intriguing topic in condensed matter physics that has attracted continuous interest for many decades [1]. In frustrated systems, such as triangular- or kagome-lattice antiferromagnets (TLAF or KLAF), because of the competing interactions, conventional magnetic long-range order was supposed to be strongly suppressed; in KLAF, several intriguing quantum disordered states are proposed theoretically, whereas recent study indicates that noncollinear 120° spin order may be realized even in the quantum limit (S = 1/2) for TLAF [2]. Recently the study on the frustrated magnetism has expanded to cluster magnetic compounds where the magnetic moment is delocalized over a group of atoms, called

a cluster, instead of being localized on a single atom. Compared to single ion magnets, cluster magnets tend to have a lesser on-site Coulomb repulsion U , as the unpaired electron responsible for the magnetism may spread much widely, making cluster magnets also a platform to study Mott-insulator physics. One group of cluster magnets is the family of transition metal trimer compounds M_3X_8 , (M = transition metal, X = anion). The pioneering compound of this group where geometric frustration was first studied is $LiZn_2Mo_3O_8$ (LZMO). This compound has magnetic Mo_3O_{13} clusters forming triangular lattice planes that are stacked with the layers of Li^+ and Zn^{2+} ions in between. Ideally, the total electronic configuration of the system is such that one unpaired electron will be localized on each Mo_3O_{13} cluster ($[Mo_3]^{11+}$, S = 1/2). The magnetic susceptibility on LZMO shows two distinct temperature ranges with two different moment sizes. With this fact together with the lack of magnetic order down to T = 0.05 K, it was inferred that an intriguing condensed valence-bond state is formed in LZMO at low temperatures [3].

If the compound certainly has the stoichiometry composition $LiZn_2Mo_3O_8$, then all the Mo_3O_{13} clusters will have S = 1/2 quantum spins, and hence this system may be an ideal quantum TLAF. However, LZMO has chemical disorder of Li and Zn atoms. This easily leads to off-stoichiometry that will introduce hole doping to Mo_3O_{13} resulting in non-magnetic clusters. Indeed, it was shown that the chemical compositions of the samples used in the earlier work may deviate from the ideal one even in their neutron diffraction results [3,4]. This casts serious doubts on the compositional reliability of the earlier work, and consequently to the condensed valence-bond state conjectured there as it totally relies on the formation of the ideal TLAF in this material.

In view of the above incomplete situation for the LZMO research, we have undertaken the thorough solid-state

chemistry research to control the composition of the LZMO compound. Using the compositionally well-characterized samples prepared in this work, we have conducted various bulk magnetic property measurements. In addition, with the sample which has the composition closest to the stoichiometry, we have performed both polarized and un-polarized neutron scattering experiments. Those results strongly suggest that the true ground state of the ideal LZMO can be rather simple dimer singlets than the condensed valence-bond state conjectured earlier.

EXPERIMENTAL

The polycrystalline samples of different compositions $Li_{1+x}Zn_{2-y}Mo_3O_8$ were prepared by solid-state-reaction technique with improved reaction condition. Crystal structure and chemical compositions were investigated using the inductively coupled plasma atomic emission spectroscopy (ICP), x-ray powder diffraction (XPD) and neutron powder diffraction (NPD). Bulk properties were characterized by measuring high-field magnetization (IMR), electron spin resonance (IMR), specific heat (ISSP), and magnetic susceptibility (IMRAM). Inelastic neutron scattering experiments were performed using the High Resolution Chopper spectrometer (HRC) at J-PARC, Polarized Neutron Triple-Axis spectrometer (PTAX) at HFIR, ORNL, and Hybrid Spectrometer (HYSPEC) at SNS, ORNL.

STOICHIOMETRY CONTROL OF LZMO

Condition for the solid-state-reaction for preparing LZMO was first revisited. Use of MoO_3 together with MoO_2 instead of just MoO_2 greatly reduces the secondary phase formation. The combined ICP-XPD-NPD characterization confirms the compositions of the primary and secondary phase, as well as the ratio of them, which has never been achieved in the earlier work. By this improvement, we could obtain samples with wide hole doping range $0.4 < p < 0.8$. We emphasize that $p = 0.78(15)$ is much closer to the ideal composition ($p = 1$) than the sample used in the earlier work ($p = 0.54(8)$ in our re-estimation).

MAGNETIZATION MEASUREMENT OF THE SERIES OF LZMO WITH DIFFERENT *p*

The magnetic susceptibility measurements were carried out for all LZMO samples with the spin 1/2 concentration per Mo_3O_{13} cluster ranging in $0.4 < p < 0.8$. It can be seen for samples with $p < 0.6$ that the inverse susceptibility exhibits two linear regions, *i.e.* the high temperature ($T > 150$ K) and low-temperature ($T < 100$ K) regions, being very similar behavior observed in the earlier work. On the other hand, when p becomes close to the unity (ideal value), clearly distinct behavior shows up in the high-temperature region around $T = 200$ K, which is a very broad peak with decreasing magnetic susceptibility for decreasing temperature.

The temperature dependence of the magnetic susceptibility for the ideal composition can be well reproduced by assuming the three components: (i) lowest temperature upturn obeying the Curie law ($\chi \propto C/T$); (ii) weak upturn below $T \approx 50$ K obeying Cuire-Weiss law ($\chi \propto C/(T - \theta)$); (iii) broad peak behavior which can be well accounted for the dimer susceptibility ($\chi \propto 1/T\,(3 + e^{J'/T})^{-1}$). The above three-component model was also used for all the samples with different p; it satisfactorily reproduces the magnetic susceptibility and the (number) fractions for the magnetic moments participating in the three components were estimated.

From the number fractions, we found that as the system becomes closer to the ideal composition, the fraction of the dimer components increases, whereas the other two components decrease. This strongly suggests that the intrinsic magnetism of LZMO is dimer formation, not the condensed valence-bond state as conjectured earlier. On the other hand, the two-temperature-region behavior reproduced in the samples with p away from unity is found to originate from the weakened dimer contribution, which accidentally forms linear inverse susceptibility in the high-T range.

In the thesis, we also discuss other bulk property measurements, such as high-magnetic-field magnetization, ESR and

specific heat, which are mostly consistent with the above three-component model.

NEUTRON SCATTERING

Using the best composition sample (p = 0.78), we have performed several neutron scattering experiments. In the HRC experiment we have clearly observed enhancement of inelastic signal at T = 5 K around $\hbar\omega$ ~ 20 meV in the low-Q region (Q < 1 Å^{-1}), where magnetic signal should be located due to the quickly decreasing magnetic form factor. In view of the temperature dependence, as well as its Q dependence, we believe the 20 meV peak is of magnetic origin. Furthermore, since the energy splitting is quite close to that estimated in the magnetic susceptibility study, this would be the singlet-triplet excitation from the dimers formed in the near-ideal LZMO compound.

We have also performed neutron scattering in the low-energy region, and the results are basically consistent with the three-component model; we have observed weakly correlating fluctuations in the low-energy region, which can be the same as those reported in the earlier neutron scattering study.

DISCUSSION

The dimer may be formed along the inter-layer c-direction, in striking contrast to the earlier conjecture of intra-layer dimers. The p dependence of the number fraction may be related to the probability of finding two S = 1/2 spins along the c-direction forming a dimer. Quantum chemistry calculation also suggests singlet-triplet excitation may be possible in a reasonable energy splitting (~10 meV). Hence, we now speculate that the dimers may be formed in the vertical direction, which is indeed, related to the bilayer nature of the crystal structure.

Nonetheless, detailed microscopic (electronic) understanding of the mechanism which makes inter-layer interaction much stronger than the intra-layer interaction is totally unclear, and further study to confirm the bilayer dimer formation is apparently necessary.

CONCLUSION

In this work, we found a method to improve the stoichiometry to p = 0.78(15) in LZMO which is much closer to the ideal composition (p = 1) than the sample used in the earlier work. We found that the magnetic susceptibility of the off-stoichiometric LZMO can be explained by three different magnetic components. One of the components, dimer formation, seems to become dominant over the two other magnetic components as p is increased closer to the ideal value. This suggests that the intrinsic ground-state of the stoichiometric LZMO is dimer singlet formation instead of the condenced valence-bond state conjectured in earlier work. By using inelastic neutron scattering we observed magnetic excitations with energy splitting close to the singlet-triplet splitting energy estimated in the magnetic susceptibility.

REFERENCES

[1] L. Balents, Nature 464 (2010) 199−208.

[2] D. A. Huse, V. Elser, Phys. Rev. Lett. 60 (1988) 2531−2534.

[3] J. P. Sheckelton, J. R. Neilson, D. G. Soltan, T. M. McQueen, Nat. Mater. 11 (2012) 493496.

[4] J. P. Sheckelton, J. R. Neilson, T. M. McQueen, Mater. Horizons 2 (2015) 76−80.

PUBLISHED ARTICLES

[1] K. E. Sandvik, D. Okuyama, K. Nawa, M. Avdeev, T. J Sato, J. Solid State Chem. 271 (2019) 216−221.

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論文審査の結果の要旨

Kim Eric Andreas SANDVIK 氏提出の論文は $S = 1/2$ 二層三角格子反強磁性体 $LiZn_2Mo_3O_8$ （以後 LZMO）の化学量論比の制御とスピン励起の観測に関するものである。量子三角格子反強磁性体は量子性、低次元性、幾何学的フラストレーションの相乗効果による興味深い基底状態形成が期待されたが、近年自明な磁気秩序状態形成が明らかになってきた。一方で、Mo_3 クラスターが有効スピン $S = 1/2$ の三角格子反強磁性体を形成する本物質では、電荷揺らぎによる非自明磁気基底状態の形成が期待される。

本論文ではまず LZMO の試料合成法改良が報告された。過去の研究で用いられた LZMO では約 46%の Mo_3 クラスターが非磁性状態であると推定される。SANDIVK 氏は合成法精査により、約 78%の Mo_3 クラスターが磁性状態にある良質な試料を得ることに成功した。更にこの合成方法では欠陥を導入することなく Li/Zn 比制御が可能である。

続いて、上述試料を用いたバルク磁気特性が報告された。高磁場磁化過程と低磁場磁化温度依存性を詳細に解析することで、本物質の磁気揺らぎが、孤立成分、弱く反強磁性相関する成分、および反強磁性シングレット 2 量体成分の 3 成分で理解できることが示された。各成分の体積分率のホール濃度依存性から、理想 LZMO 試料においてはシングレット 2 量体が支配的であると提案された。

さらに、最も理想組成に近い試料を用いた中性子非弾性散乱実験が行われた。本研究では、Mo_3 クラスターからの磁気散乱が計測可能と予想される低角領域が初めて測定されたが、その結果 20 meV 程度のギャップを伴う磁気励起が観測され、これが 2 量体起源の励起であると議論された。

最後に 2 量体形成の起源として、類似物質との比較、確率論的考察および量子化学計算から層間 2 量体形成機構が提案された。

これらの研究結果は、Mo_3 クラスターからなる量子三角格子反強磁性体の新しい基底状態を提案するものとして大きな意義を持つものである。また試料作成から中性子非弾性散乱実験まで多様な実験を独力で遂行したことは本人が自立して研究活動を行うのに必要な高度な研究能力と学識を有することを示している。従って、SANDVIK 氏提出の論文は博士（理学）の学位論文として合格と認める。